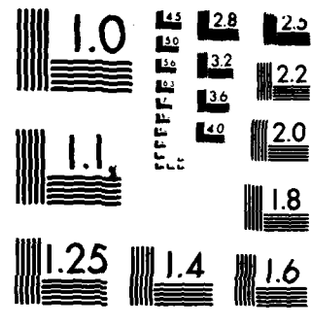
AD-A142 249 ION CONDUCTION POLY(VINYL ACETATE)(U) HUNTER COLL NEW 1/1
YORK DEPT OF PHYSICS AND ASTRONOMY
M C WINTERSGILL ET AL. JUN 84 N00014-84-K-0010

UNCLASSIFIED F/G 20/3 NL

END
DATE FILMED
7-84
DTIC



OFFICE OF NAVAL RESEARCH
Contract N00014-84K-0010
Task No. NR 359-841
Technical Report No. 1

ION CONDUCTING POLY(VINYL ACETATE)

by

M.C. Wintersgill, J.J. Fontanella, J.P. Calame
S.G. Greenbaum, and C.G. Andeen

Prepared for Publication
in
Journal of the Electrochemical Society

Hunter College of CUNY
Department of Physics
New York, N.Y. 10021

April 1984

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: 1	2. GOVT ACCESSION NO.: AD-A142249	3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): ION CONDUCTING POLY(VINYL ACETATE)		5. TYPE OF REPORT & PERIOD COVERED: Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): M.C. Wintersgill, J.J. Fontanella, J.P. Calame, S.G. Greenbaum, C.G. Andeen		8. CONTRACT OR GRANT NUMBER(s): N00014-84K-0010
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Hunter College of CUNY, Department of Physics and Astronomy, New York, NY 10021		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 359-841
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research/Code 413, 800 N. Quincy St., Arlington, VA 22217		12. REPORT DATE: June 1984
		13. NUMBER OF PAGES: 7
14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release and sale.
Distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The paper will appear in Journal of the Electrochemical Society.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Solid electrolytes, polymer electrolytes, poly(vinyl acetate), ionic conductivity, nuclear magnetic resonance

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

AC conductivity and ^{7}Li NMR measurements of poly(vinyl acetate) complexed with $LiClO_4$ are reported. The observations of temperature-activated conductivity, and ^{7}Li motional narrowing and rapid spin-lattice relaxation rates are consistent with fast ion transport in the complex. In addition, a lithium cell utilizing the complex as the electrolyte exhibited an open circuit voltage of ~3V while no voltage was detected for an identical cell with a pure poly (vinyl acetate) electrolyte.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

J. Electrochem Soc.
Submitted
(accepted)

ELECTRICALLY CONDUCTING POLY(VINYL ACETATE)

M.C. Wintersgill, J.J. Fontanella,* J. P. Calame
Physics Department
U.S. Naval Academy
Annapolis, MD 21402

S.G. Greenbaum
Dept. of Physics and Astronomy
Hunter College of CUNY
New York, NY 10021

C.G. Andeen
Physics Department
Case Western Reserve University
Cleveland, OH 44106

INTRODUCTION

Electrically conducting polymers have recently been the subject of intense interest. Polyacetylene has been widely studied as an electronic conductor. Ionic conductors include poly(ethylene oxide) (1), poly(propylene oxide) (2), polyacrylonitrile (3), poly(vinylidene fluoride) (3), poly(tetramethylene oxide) (4) and poly(ethylene succinate) (5). In the present note, the observation of electrically conducting poly(vinyl acetate) (PVAc) is reported. Ionic conduction is inferred from the data.

EXPERIMENT AND RESULTS

PVAc (MW 1.5×10^6) was obtained from Polysciences, Inc. PVAc and $LiClO_4$ in the ratio 8:1 were dissolved in methanol then dried in air on a teflon plate at about 55°C. The result was a brittle, clear solid at room temperature. Pure PVAc was prepared by the same method for comparison. Aluminum electrodes were then evaporated onto the faces of several samples and audio frequency complex impedance measurements were performed in a vacuum at temperatures from 5.5 K to 380 K using techniques described elsewhere (6). The results for one frequency (100 Hz) are shown in figure 1. Four other frequencies from 100-10^4 Hz gave similar results and are omitted for clarity. It is seen that the d.c. conductivity of the $LiClO_4$ complexed material at 100°C is about three orders of magnitude larger than that of the pure material and increases exponentially with an activation energy of about 2.1 eV. However, at about 50°C the a.c. conductivity of the pure material (a.c. loss due to the relaxation peak associated with the glass transition) is slightly greater than that for the complexed material at the same temperature. The glass

---

* Electrochemical Society Active Member
Key words: polymer electrolytes
electrical conductivity.

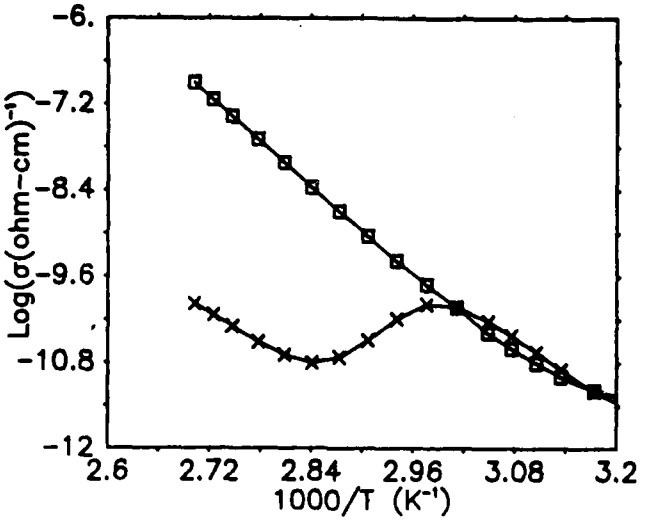


Fig. 1. $Log(\sigma(ohm\text{-}cm)^{-1})$ vs. $1000/T\ (K^{-1})$ for pure PVAc (x) and $PVAc_8\text{-}LiClO_4$ (□) at 100 Hz.

transition in the complexed material is shifted to higher temperatures where it is probably masked by the d.c. conductivity. This temperature shift is confirmed by differential scanning calorimetry (DSC) studies. The DSC results together with further electrical relaxation studies will be presented elsewhere.

In order to gain further information concerning this material, ^7Li NMR linewidth and spin-lattice relaxation T_1 measurements were conducted at 155 MHz with a JEOL GX400 NMR spectrometer, after sealing the sample in an evacuated quartz tube. Over the temperature range studied, the ^7Li spectra exhibit a single absorption with no apparent quadrupolar broadening (as deduced by the appropriate $\pi/2$ pulsewidth condition). The temperature dependence of the full-width-at-half-maximum (FWHM)-linewidth is shown in figure 2 (triangles). The T_1-recovery process was found to be slightly non-exponential, which may indicate the presence of more than one relaxation time. However, no significant temperature dependence of the recovery profile was observed, which allowed the use of an "effective T_1," defined as the time required

for the magnetization to recover 63% of its maximum value. A plot of T_1 (effective) vs. 1000/T also appears in Figure 2 (squares). The value of the "rigid linewidth" (4.4 kHz), which occurs below about 220K and the observed motional narrowing behavior bear a close similarity to results reported for PEO-Li^+-based materials,[7,8] which suggests a comparable degree of Li^+ and/or polymer chain motion in $PVAc_8$-$LiClO_4$. There are, unfortunately, no T_1 measurements above 383K at present, but it is likely that a T_1 minimum would occur at or near the melting point of the complex. T_1 does, however, exhibit Arrhenius behavior throughout the motional narrowing region (above room temperature) with an activation energy of 0.14±0.03 eV. This small value presumably reflects localized motion with a correspondingly small potential energy barrier. The relation between the apparent localized process and motion resulting in long-range transport is not clear at the present time.

Finally, the following cell was constructed: $Li/PVAc_8$-$LiClO_4/MnO_2$-C-PVF_2. The composition of the cathode was about 82% MnO_2, 9.6% C and 8.4% PVF_2 by weight. The materials were hot-pressed at about 205°C to form a conducting disk about 2.54 cm in diameter and 1 mm thick. The polymer film was about 0.4 mm thick and 2 cm in diameter, while the lithium electrode was about 1 mm thick with a diameter of about 1.2 cm. The three disks were spring loaded into a cell under an argon atmosphere. The cell was not hermetically sealed. Although the present data were obtained with the cell in air, similar results were obtained when the experiment was carried out under vacuum. The discharge characteristics are shown in figure

3. Further tests showed that with a 100kΩ load, the voltage decreased gradually from 1.8V to 0.9V over a period of 16 hours. The cell failed at that time. While the discharge characteristics of the present cell are not particularly impressive, it should be emphasized that no attempt was made to optimize the performance of the cell. The construction of the cell was rather primitive and, for example, a higher operating temperature or thinner polymer would decrease the internal resistance of the cell. The "open circuit" voltage (the resistance of the Keithley 195 DMM is about 10^6 ohms) is about 3.04 volts, which is not unreasonable for a cell of this type. Further, the initial internal resistance of the cell, was about 93 kΩ and was about 85 times larger than the resistance predicted from the a.c. conductivity measurements described above. While there is considerable uncertainty in the latter value due to the ambiguities in the geometry of the cell, it is clear that the internal resistance of the cell is larger than the a.c. resistance of the bulk polymer material. This is not surprising since, for example, anions as well as cations may be contributing to the a.c. conductivity, thus giving rise to a lower a.c. resistance. Finally, a similar cell was constructed using a pure PVAc film in place of the PVAc-$LiClO_4$. No voltage was detected for this cell.

All results are consistent with ion transport.

ACKNOWLEDGMENTS

This work was supported in part by the Office of Naval Research. S.G.G. also acknowledges support from the Research Corporation.

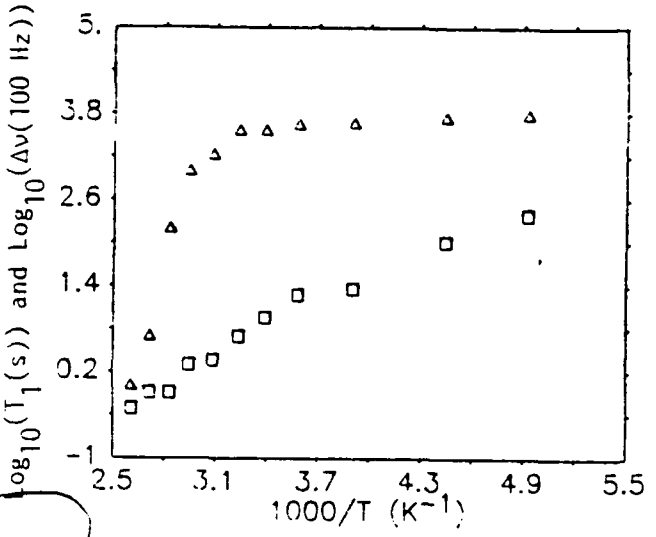


Fig. 2. Temperature dependences of ^7Li FWHM linewidth (△) and effective T_1 (□).

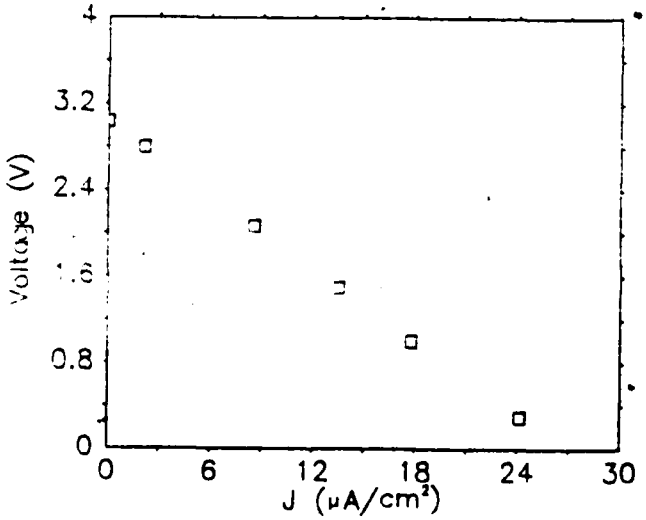


Fig. 3. Voltage (V) vs. J($\mu A/cm^2$) for the cell: $Li/PVAc_8-LiClO_4/MnO_2-C-PVF_2$ at 125°C.

REFERENCES

1. P. V. Wright, Br. Polym. J., 7, 319 (1975).
2. M. B. Armand, J. M. Chabagno and M. J. Duclot, in: Fast ion transport in solids, eds. P. Vashishta, J. N. Mundy and G. K. Shenoy (North Holland, Amsterdam, 1979) p. 131.
3. M. Watanabe, M. Kanba, H. Matsuda, K. Tsunemi, K. Mizoguchi, E. Tsuchida and I. Shinohara, Makromol. Chem. Rapid Commun., 2, 741 (1981).
4. M. Watanabe, K. Nagaoka, M. Kanba and I. Shinohara, Polym. J., 14, 877 (1982).
5. R. Dupon, B. L. Papke, M. A. Ratner and D. F. Shriver, Submitted for publication.
6. J. J. Fontanella, M. C. Wintersgill, J. P. Calame and C. G. Andeen, Solid St. Ionics, 8, 333 (1983).
7. F. L. Tanzella, W. Bailey, D. Frydrych, G. C. Farrington, H. S. Story, Solid St. Ionics, 5, 681 (1981).
8. A. Killis, J. F. LeNest, A. Gandini, H. Cheradame, J. P. Cohen-Addad, Polymer Bull., 6, 351 (1982).

DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

DL/413/83/01
359/413-2

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. David Aikens
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. A. P. B. Lever
Chemistry Department
York University
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 6343, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
and Power Sources Division
Naval Weapons Support Center
Crane, Indiana 47522

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
K33/281
5600 Cottle Road
San Jose, California 95193

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson
NAVSEA-56Z33 NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. D. Cipris
Allied Corporation
P.O. Box 3000R
Morristown, New Jersey 07960

Dr. M. Philpott
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Donald Sandstrom
Department of Physics
Washington State University
Pullman, Washington 99164

Dr. Carl Kannewurf
Department of Electrical Engineering
and Computer Science
Northwestern University
Evanston, Illinois 60201

DL/413/83/01
359/413-2

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. M. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
M.S. 6B025 Forrestal Bldg.
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. William Ayers
ECD Inc.
P.O. Box 5357
North Branch, New Jersey 08876

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Corporation
111 Chapel Street
Newton, Massachusetts 02158

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southamptor
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Denton Elliott
Air Force Office of Scientific
Research
Bolling AFB
Washington, D.C. 20332

Dr. R. Nowak
Naval Research Laboratory
Code 6130
Washington, D.C. 20375

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

DL/413/83/01
359/413-2

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southampton SO9 5NH
United Kingdom

Dr. T. Katan
Lockheed Missiles and
Space Co., Inc.
P.O. Box 504
Sunnyvale, California 94088

Dr. D. N. Bennion
Department of Chemical Engineering
Brighma Young University
Provo, Utah 84602

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Mr. Joseph McCartney
Code 7121
Naval Ocean Systems Center
San Diego, California 92152

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. H. Richtol
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
Science Department
Lawrence Livermore National Lab.
Livermore, California 94550

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. G. Goodman
Johnson Controls
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201

Dr. B. Brummer
EIC Incorporated
111 Chapel Street
Newton, Massachusetts 02158

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Electrochimica Corporation
Attn: Technical Library
2485 Charleston Road
Mountain View, California 94040

Library
Duracell, Inc.
Burlington, Massachusetts 01803

Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706

DL/413/83/01
359/413-2

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. Robert Somoano
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus
NASA Headquarters
M.S. RTS-6
Washington, D.C. 20546

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. M. Tachikawa
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Dr. Theodore Beck
Electrochemical Technology Corp.
3935 Leary Way N.W.
Seattle, Washington 98107

Dr. Farrell Lytle
Boeing Engineering and
Construction Engineers
P.O. Box 3707
Seattle, Washington 98124

Dr. Robert Gotscholl
U.S. Department of Energy
MS G-226
Washington, D.C. 20545

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402

Dr. Martha Greenblatt
Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Dr. John Wasson
Syntheco, Inc.
Rte 6 - Industrial Pike Road
Gastonia, North Carolina 28052

Dr. Walter Roth
Department of Physics
State University of New York
Albany, New York 12222

Dr. Anthony Sammells
Eltron Research Inc.
710 E. Ogden Avenue #108
Naperville, Illinois 60540

Dr. W. M. Risen
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymer Science and Standards
Division
National Bureau of Standards
Washington, D.C. 20234


DA
FILM
7